

Conductance quantization and electron resonances in sharp tips and atomic-size contacts

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The electronic and transport properties of atomic-size contacts are analyzed theoretically using a self-consistent tight-binding model. Our results show that, for *s*-like metals, a sufficiently narrow contact exhibits well defined resonant states at the Fermi energy, spatially localized in the neck region. These states are robust with respect to disorder and provide a simple explanation for the observed tendency to conductance quantization. It is also shown that these properties disappear for a sufficiently large contact area. The possible relevance of the resonant states in scanning tunneling spectroscopy using sharp tips is briefly discussed.

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The electronic and transport properties of metallic point contacts have received a renewed attention with the advent of controllable atomic-size contacts that can be produced using the scanning tunneling microscope [1] and the more recently developed mechanically controllable break junctions [2].

By means of these techniques, conductance steps in both the jump-to-contact and jump-to-tunnel processes are generally observed in the experiments [1–3]. The steps have been correlated with abrupt atomic rearrangements taking place in the neck region [1]. An important issue, still not completely understood [4], is whether these steps should correspond to quanta of the conductance. What seems clear from the experimental data is that, for metals having basically an *s*-character (*Na*, *Au*, *Ag*, *Cu*, etc), the value of the first conductance jumps tends to be very close to a multiple of the quantum of conductance $2e^2/h$, while the higher conductance steps exhibit a less reproducible behavior [3]. On the other hand, transition metals like *Ni* and *Pt* exhibit a broad distribution of the first conductance step, which can be larger than $2e^2/h$ by a factor between 1 and 3. This effect has been attributed to the role played by the *d*-electrons of these materials that open new channels to the electronic conduction [5].

Theoretically, different authors have analyzed the mechanical properties of these atomic-size contacts using molecular dynamics simulations [6] as well as their transport properties by means of tight-binding [7] and free-electron calculations [8]. The molecular dynamics simulations show that a one-atom point contact is a stable configuration [6] and several theoretical models have predicted that the maximum value of the conductance is $2e^2/h$ for a single atom contact with one orbital per site [9–12]. Nevertheless, it is not yet clear why the first step quantization should be observed in such a reproducible way for simple metal contacts. Free-electron calculations have tried to explain this fact by using an adjustable contact cross section, πr_0^2 , taking into account the size of the contact atom [8]. However, the results of this model seem to depend critically on the ratio λ_F/r_0 . On the other hand, conductance quantization seems to be even

much harder to obtain using a tight-binding description of realistic models for the contact atomic structure [7].

In this work we address this problem by focusing our attention on the electronic properties of very sharp tips and narrow atomic-size contacts. We concentrate our discussion on metals having essentially an *s*-like band character which, as commented above, are the ones displaying conductance quantization in a more reproducible way. We shall show that for sufficiently sharp tips there appear narrow electron resonances which are spatially localized around the apex atom. As discussed below, these states could certainly play an important role in scanning tunneling spectroscopy. When forming an atomic contact, and due to charge neutrality conditions, the Fermi level is pinned at one of these resonances, explaining in a natural way conductance quantization at the first plateaux. Furthermore, we shall show that these results are robust with respect to the inclusion of disorder.

In order to describe the electronic and transport properties of an atomic-size tip or contact, we shall use an atomic orbital basis leading to a tight-binding Hamiltonian with the form

$$\hat{H} = \sum_{i\alpha,\sigma} \epsilon_{i\alpha} c_{i\alpha,\sigma}^\dagger c_{i\alpha,\sigma} + \sum_{i\alpha \neq j\beta,\sigma} t_{i\alpha,j\beta} c_{i\alpha,\sigma}^\dagger c_{j\beta,\sigma}, \quad (1)$$

where indexes i, j run over the atomic sites and α, β denote the different atomic orbitals at each site. For representing simple metals, we shall first consider the case of a single *s* orbital per site and then discuss qualitatively the effect of including *p* orbitals. The hopping elements $t_{i\alpha,j\beta}$ are assumed to connect first-neighboring sites, and can be taken from fittings to ab-initio electronic band calculations [13]. When considering a single orbital per site the relevant parameter is the first-neighbors hopping element t , which is of the order of 1eV for typical metals. The diagonal elements $\epsilon_{i\alpha}$ will be modified self-consistently to achieve local charge neutrality, which is a reasonable assumption for a metallic system [14].

The first step in this analysis is to show that sharp resonant states can exist in a tip geometry (i.e., a semi-infinite arrangement of atoms like the ones depicted in

Fig. 1) provided it is sufficiently sharp. Physical intuition suggests that metallic atomic tips and contacts would most likely have a close packed structure. This is supported by computer simulations [6] at least for sufficiently large temperature, when the tendency to minimize the contact energy can be developed. We thus first consider tip geometries which can be grown from an apex atom along different crystallographic orientations on an fcc lattice, adding the first neighboring sites when going from one atomic layer to the next. In this way, when the (111) direction is chosen, one obtains a very sharp tip with an opening angle of $\sim \pi/4$; we shall also consider the (100) direction that leads to a tip with a larger opening angle of $\sim \pi/2$.

We have studied the electronic structure of these tips by first considering small clusters around the apex atom with an increasing number of layers n . The atoms on the last layer are connected to a Bethe lattice structure that simulates the bulk DOS. The inset of Fig. 1 shows the LDOS at the tip apex atom as a function of n for a (111) tip. These results show that, as n increases, the spectral density for $E \geq 0$ tends to concentrate into two sharp resonances at $E \sim 0.4t$ and $\sim 1.5t$. The LDOS below $E = 0$ is, however, much more sensitive to the number of layers in the cluster and converges slowly to a continuous spectrum, as corresponds to extended states. This part of the spectrum is thus not completely well described by a small cluster calculation.

A more efficient algorithm for calculating the LDOS at a given atom is provided by the recursion method [15]. Using this method one obtains an expansion of the local Green functions as a continued fraction

$$G_{j\alpha,j\alpha}(\omega) = \frac{1}{\omega - a_0 - b_0^2 g_1(\omega)},$$

$$g_n(\omega) = \frac{1}{\omega - a_n - b_n^2 g_{n+1}(\omega)} \quad (2)$$

where the coefficients a_n, b_n are obtained by generating a new basis recursively [15] taking a generic local orbital $|j\alpha\rangle$ as the initial state. Notice that the coefficients a_n, b_n define an effective 1D tight-binding Hamiltonian with diagonal levels a_n and hopping elements b_n . When starting from the apex site ($j = 0$), the n site in this effective semi-infinite chain corresponds to a state of the tip having a finite weight on the first n layers.

The LDOS at the tip apex site obtained for the (100) and (111) grown tips are shown in Fig 1. As can be observed, the less sharp tip exhibits a smooth LDOS resembling the fcc bulk DOS. On the contrary, for the sharper (111) case the LDOS is qualitatively different, exhibiting narrow resonances in agreement with those found in the finite cluster calculation.

The appearance of these resonances can be understood in the following way: while in a blunt tip the local environment around the apex atom is similar to that of a flat surface tending quickly to that of the bulk, in the sharp (111) structure it converges more slowly and thus

the apex region, which is much more weakly coupled to the bulk, can exhibit resonant states. This is reflected in the different evolution of the a_n, b_n coefficients towards their bulk values ($a_\infty = -4t, b_\infty = 4t$), as shown in Fig. 2. Furthermore, the coefficients of the (111) case exhibit significant fluctuations which decrease rather slowly with increasing n . The effective 1D Hamiltonian for this case thus describes the motion of an electron in a fluctuating potential, which displays a region of localized states. In fact, the wave functions of the effective 1D problem that correspond to resonant states are strongly localized around the tip apex, with a typical localization length corresponding to a few atomic layers.

Broadening of the resonant levels is mainly introduced by topological disorder, which has been simulated by allowing the hopping elements to fluctuate randomly within a certain range $t \pm \Delta t$. The broadening can be understood by noticing that the effect of disorder is to reduce the fluctuations in the effective 1D parameters a_n and b_n due to a loss of coherence between the different interfering paths from the tip apex to a given layer. This is illustrated in the inset of Fig. 2. We have found, however, that this effect is never very large and the resonances remain well defined (even for $\Delta t \sim t$, which is much larger than the expected fluctuations on t , the peak labeled as B in Fig. 1 acquires only a small broadening $\sim 0.1t$).

The relevance of these resonant states becomes clear after realizing that, for a (111) tip, the Fermi level is located above the smooth part of the apex atom LDOS. This is so because, the total charge per spin on the smooth LDOS is less than 0.5 electrons and E_F turns out to be located between the two resonances A and B, as indicated in Fig. 1. Accordingly, these resonances should be observed in Scanning Tunneling Spectroscopy when using sufficiently sharp tips. Notice that typical tips are, however, made of transition metals like W for which the simplified one orbital per site model is not sufficient. We have performed specific calculations for W tips including d orbitals and found that they should also exhibit resonant states in certain conditions. This has been confirmed by recent experiments [16] and might clarify an existing controversy regarding the electronic structure of W-tips [17].

It seems then plausible that the same kind of resonant states could be present in a one-atom neck geometry, which can be viewed as two tips connected by a central common atom. This model geometry can either represent the atomic contacts that are formed with the break-junction technique or by using the STM techniques after repeated cycles of plastic deformation [18]. The self-consistent LDOS at the central atom and on a neighboring layer of a (111) neck are shown in Fig. 3. As expected, they exhibit resonant states, which are, however, shifted from their position in the tip case. The LDOS at the central atom is dominated by a clear resonance at $E \sim 0.35t$, whereas the resonance at E_F is mainly localized on the first neighboring layers. The spatial variation

of this resonant state is depicted in the lower inset of Fig. 3. The broadening of these states due to topological disorder is twice as large as the one found for the tip; thus the maximum broadening is around $0.2t$ and the typical line-width is $\sim 0.1t$, i.e. around 0.1eV for simple metals.

The existence of a half-filled resonant state for the (111) neck geometry provides a strong mechanism for explaining the almost perfect quantization of the conductance at the first plateau. In fact, the conductance of this single atom contact is given by [19]

$$g = \frac{2e^2}{h} \{ 4\text{Im}\Sigma_R(E_F)\text{Im}\Sigma_L(E_F)|G(E_F)|^2 \} \quad (3)$$

which behaves as the usual resonant tunneling transmission formula around a resonant state [19]. We use the zero temperature conductance, as the line-width of the resonant state at E_F , although small compared to t , can be expected to be much larger than $k_B T$, even at room temperature. $\Sigma_R(\omega)$ and $\Sigma_L(\omega)$ are the self-energies of the right and left sides of the contact projected on the central atom; $G(\omega)$ is the local Green function on this atom, given by $1/[\omega - \epsilon_0 - \Sigma_L(\omega) - \Sigma_R(\omega)]$. As the Fermi energy is located at the center of a sharp resonance, Eq. (3) takes the form $g = (8e^2/h)x/(1+x)^2$, where $x = \text{Im}[\Sigma_R(E_F)]/\text{Im}[\Sigma_L(E_F)]$. For the perfect (111) atomic contact $x = 1$, and $g = 2e^2/h$. Fluctuations in the atomic positions introduce variations in the values of $\text{Im}[\Sigma_{R,L}(E_F)]$, but, as far as the resonance is well defined, charge neutrality keeps it centered around E_F . One should notice, however, that around $x = 1$, g changes very slowly with x ; thus, for a deviation as large as $x = 2$, $g \simeq 1.8e^2/h$, i.e. 90% of the quantum unit. Sharp resonances thus provide a strong mechanism for the conductance quantization on the first plateau [20]. In the opposite case of a smooth LDOS (like in the (100) case) perfect transmission and maximum conductance only occur at certain energies which *do not*, in general, correspond to E_F .

The previous analysis has been restricted to one-atom contacts. It is also worth considering the effect of increasing the contact area. For instance, three atom contacts can be obtained from the initial (111) structure by removing the central atom, thus defining the sequence ...6 – 3 – 3 – 6..., where the numbers give the atoms per layer. This geometry also exhibits sharp resonances in the neck LDOS, allowing us to predict, by a simple electron counting argument, a conductance of $2 \times (2e^2/h)$ (E_F lies in the middle of a two-fold degenerate level). A different three-atom contact configuration like ...6 – 3 – 6... would correspond to a conductance of $3 \times (2e^2/h)$. Can we expect to obtain increasing conductance quanta, $n \times (2e^2/h)$, when the neck contact area is progressively increased? The arguments given in this work suggest that the limit to a well defined conductance quantization should appear for a contact size for which the resonant states at E_F begin to disappear. In this respect, we have analyzed the LDOS of contacts with an

increasing number of atoms in the neck section and found that for sections of the order or larger than six atoms the resonances become too broad to be resolved.

So far we have neglected the effect of p orbitals. We have also performed calculations including them but still assuming to have a single electron per site. Alkali atoms are typical cases of this situation but also *Au*, *Ag* and *Cu* can be well represented by this model. Our results show that there is still a narrow resonance at the Fermi level having mainly an *s*-character, giving further support to the main argument of this work. For metals like *Al*, having more conduction electrons per atom and a larger *p*-character at E_F , the resonances become very much broadened. As a consequence we would not expect the conductance quantization of the first plateau to be as robust in these metals as in the previous cases, in agreement with the experimental evidence [3].

In conclusion we have shown that, for metals having mainly an *s*-character and for sufficiently narrow tips, resonant electron states appear at and around E_F , spatially localized at the tip apex. The inclusion of the discrete atomic structure is *essential* for obtaining these states, which would not be present in a jellium constriction model. When a single atom contact is formed, E_F is pinned by one of those resonances and a quantum unit conductance is obtained, a result that is shown to be robust with respect to the inclusion of disorder. By increasing the contact area, the conductance is expected to increase by multiples of the quantum unit as far as those resonant states still exist at E_F . A limit to this increase is set by the disappearance of the resonances due to the increase of the contact size. Our calculations show that for a contact area of six atoms the resonances become too broad and explain why in most experiments the conductance quantization $n \times (2e^2/h)$ is only seen in a reproducible way for small values of n .

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FIG. 1. LDOS at the apex atom for tips grown in the (111) (full line) and in the (100) (dotted line) directions. The upper insets give a top view of the two tip geometries. In the lower inset the apex atom LDOS for small (111) clusters are shown for $n = 6, 8, 10$ and 12 layers. The two resonant states are labeled by *A* and *B*.

FIG. 2. Coefficients a_n and b_n in the continued fraction expansion of the tip apex Green function for the (111) (full line) and (100) (dotted line) geometries. In the inset the behavior of a_n with increasing amplitude of random fluctuations in the hopping parameter, Δt , is shown for the (111) case.

FIG. 3. LDOS at the central (full line) and at the first neighboring layer (dotted line) for the (111) neck geometry. The broken line gives the contact conductance. The upper inset gives a side view of the (111) neck geometry. In the lower inset the effective 1D problem wave-function corresponding to the resonant state at E_F is shown.







